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TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. §371			ATOCM 202 U.S. APPLICATION NO (If known, see 37 CFR §1.5) 09/806710
INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED	
PCT/FR00/02140	26 JULY 2000	4 AUGUST 1999	
TITLE OF INVENTION ANTISTATIC STYRENE POLYMER COMPOSITIONS			
APPLICANT(S) FOR DO/EO/US LACROIX, Christophe			
<p>Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:</p> <ol style="list-style-type: none"> <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. §371. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. §371. <input type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. §371(b) and PCT Articles 22 and 39(1). <input type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. §371(c)(2)) <ol style="list-style-type: none"> <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). <input checked="" type="checkbox"/> has been transmitted by the International Bureau. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. §371(c)(2)). <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. §371(c)(3)) <ol style="list-style-type: none"> <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). <input type="checkbox"/> have been transmitted by the International Bureau. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. <input checked="" type="checkbox"/> have not been made and will not be made. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. §371(c)(3)). <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. §371(c)(4)). <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. §371(c)(5)). <p>Items 11. to 16. below concern document(s) or information included:</p> <ol style="list-style-type: none"> <input type="checkbox"/> An Information Disclosure Statement under 37 C.F.R. §§1.97 and 1.98. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 C.F.R. §§3.28 and 3.31 is included. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. <input type="checkbox"/> A substitute specification. <input type="checkbox"/> A change of power of attorney and/or address letter. <input type="checkbox"/> Other items or information: 			

Form PTO-1390

IN THE UNITED STATES DESIGNATED/ELECTED OFFICE

International Application No.: PCT/FR00/02140
International Filing Date: 26 JULY 2000
Priority Date(s) Claimed: 04 AUGUST 1999
Applicant(s) (DO/EO/US): LACROIX, Christophe
Title: ANTISTATIC STYRENE POLYMER COMPOSITIONS

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, D.C. 20231

SIR:

Prior to calculating the national fee, and prior to examination in the National Phase of the above-identified International application, please amend as follows:

IN THE ABSTRACT

Please replace the existing Abstract with the attached Abstract of the Disclosure.

IN THE SPECIFICATION

Page 1, line 4, please delete the subheading "[Field of the Invention]".

Page 1, line 32, please delete the subheading "[Prior Art]".

Page 2, line 30, please delete the subheading "[The technical problem]".

Please replace the subheading "[Brief description of the invention]" beginning on page 3, line 10, with --Summary--.

Page 3, line 26, please delete "[Detailed description of the invention]".

IN THE CLAIMS

Please cancel claims 1-9 without prejudice or disclaimer.

Please add the following claims:

-- 10. A composition comprising, per 100 parts by weight:

99 to 60 parts of a styrene polymer (A),

1 to 40 parts of (B) + (C),

(B) being a copolymer containing polyamide blocks and polyether blocks comprising essentially ethylene oxide units $-(C_2H_4-O)-$,

(C) being a compatibilizer selected from the group consisting of: (C1) low-mass copolymers of styrene and of an unsaturated carboxylic acid anhydride, (C2) copolymers of ethylene and of an unsaturated carboxylic acid anhydride, (C3) copolymers of ethylene and of an unsaturated epoxy, (C4) block copolymers of polystyrene/polybutadiene/polystyrene or polystyrene/polyisoprene/polystyrene grafted by an unsaturated carboxylic acid or an unsaturated carboxylic acid anhydride or mixtures thereof, (B)/(C) having a weight ratio between 2 and 10.

11. A composition according to claim 10, in which (A) is polystyrene.

12. A composition according to claim 10, in which (A) is an acrylonitrile-butadiene-styrene copolymer ABS.

13. A composition according to claim 10, wherein (C) is (C1) in which (C1) is a copolymer of styrene and maleic anhydride having an average molar mass of between 800 and 10,000.

14. A composition according to claim 10, wherein (C) is (C2) in which (C2) is an ethylene-alkyl (meth)acrylate-maleic anhydride copolymer, containing from 0.2 to 10% by weight of maleic anhydride and from 0 to 40% by weight of alkyl (meth)acrylate.

15. A composition according to claim 10, wherein (C) is (C3) in which (C3) is an ethylene/alkyl (meth)acrylate/unsaturated epoxy copolymer optionally containing up to 40% by weight of alkyl(meth)acrylate and up to 10% by weight of unsaturated epoxy.

16. A composition according to claim 10, which the amount of (B) + (C), is by weight, from 5 to 20 parts per 95 to 80 parts by weight of (A).

17. A composition according to claim 10, in which the weight ratio (B)/(C) is between 4 and 6.

18. An article selected from the group consisting of film, pipe, sheets, packaging, computer casings, and telephone casings, said article comprising a composition according to claim 10.

19. A composition according to claim 10, wherein (C) comprises (C1).

20. A composition according to claim 10, wherein (C) comprises (C2).

21. A composition according to claim 10, wherein (C) comprises (C3).

22. A composition according to claim 10, wherein (C) comprises (C4).

23. A process comprising shaping a composition according to claim 10 into an article selected from the group consisting of film, pipe, sheets, packaging, computer casings, and telephone casings. --

REMARKS

A principle purpose of this Preliminary Amendment is to eliminate multiple dependent claims in order to avoid the additional fee, Applicants reserving the right to reintroduce claims to canceled combined subject matter. Another purpose is to provide editorial changes so as to comply with U.S. patent terminology. Still another purpose is to add subgeneric claims 19-22 and process claim 23.

Attached hereto is a marked-up version of the changes made to the specification and claims by the current amendment. The attached page is captioned "**Version With Markings To Show Changes Made**".

Respectfully submitted,



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ABSTRACT OF THE DISCLOSURE

A composition and articles, e.g. computer casings comprising, per 100 parts by weight: 99 to 60 parts of a styrene polymer (A), 1 to 40 parts of (B) + (C), (B) being a copolymer containing polyamide blocks and polyether blocks comprising essentially ethylene oxide units $-(C_2H_4-O)-$, (C) being a compatibilizer chosen from (C1) low-mass copolymers of styrene and of an unsaturated carboxylic acid anhydride, (C2) copolymers of ethylene and of an unsaturated carboxylic acid anhydride, (C3) copolymers of ethylene and of an unsaturated epoxy, (C4) block copolymers (C4) SBS or SIS grafted by an unsaturated carboxylic acid or an unsaturated carboxylic acid anhydride and mixtures thereof, the weight ratio (B)/(C) being between 2 and 10.

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Version With Markings To Show Changes Made

IN THE ABSTRACT

The abstract has been replaced and therefore no marked up version is necessary.

IN THE SPECIFICATION

Subheading beginning at page 1, line 4, has been deleted.

Subheading beginning at page 1, line 32, has been deleted.

Subheading beginning at page 2, line 30, has been deleted.

Subheading beginning at page 3, line 10, has been deleted and replaced with "Summary".

Subheading beginning at page 3, line 26, has been deleted.

IN THE CLAIMS

Claims 1-9 have been canceled.

New claims 10-23 have been added.

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ANTISTATIC STYRENE POLYMER COMPOSITIONS

[Field of the invention]

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The present invention relates to antistatic styrene polymer compositions and more specifically to a composition comprising a styrene polymer (A), a copolymer (B) containing polyamide blocks and polyether blocks essentially comprising ethylene oxide units $-(C_2H_4-O)-$ and a compatibilizer (C).

10

The aim of the invention is to give the styrene polymer (A) antistatic properties. The formation and retention of static-electricity charges on the surface of most plastics are known. The presence of static electricity on thermoplastic films results, for example, in these films sticking to each other, making them difficult to separate. The presence of static electricity on packaging films may cause the accumulation of dust on the articles to be packaged and thus impede their use. Styrene resins such as, for example, polystyrene or ABS are used for making casings for computers, telephones, televisions, photocopiers and many articles. Static electricity causes dust to accumulate, but above all it can damage the microprocessors or the components of the electronic circuits contained in these articles.

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The prior art has described antistatic agents, such as ionic surfactants of the ethoxylated amine or sulphonate type, which are added to polymers. However, the antistatic properties of the polymers depend on the ambient moisture and are not permanent since these agents migrate to the surface of the polymers and disappear. It has therefore been proposed to use, as antistatic agents, copolymers containing polyamide blocks and hydrophilic polyether blocks, these agents having the advantage of not migrating and therefore of giving permanent antistatic properties which are also independent of the ambient moisture.

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[Prior Art]

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Japanese Patent Application JP 60,170,646 A published on 4 September 1985 describes compositions consisting of 0.01 to 50 parts of a polyether-block-amide and 100 parts of polystyrene, these being useful for making sliding parts and wear-resistant parts. The antistatic properties
5 are not mentioned.

Patent Application EP 167,824 published on 15 January 1986 describes compositions similar to previous ones and, in one embodiment of the invention, polystyrene may be blended with a polystyrene functionalized by an unsaturated carboxylic anhydride. These compositions
10 are useful for making injection-moulded parts. The antistatic properties are not mentioned.

Japanese Patent Application JP 60,023,435 A published on 6 February 1985 describes antistatic compositions comprising 5 to 80% of polyetheresteramide and 95 to 20% of a thermoplastic resin chosen from
15 among polystyrene, ABS and PMMA, this resin being functionalized by acrylic acid or maleic anhydride. The amount of polyetheresteramide in the examples is 30% by weight of the compositions.

Patent EP 242,158 describes antistatic compositions comprising 1 to 40% of polyetheresteramide and 99 to 60% of a thermoplastic resin chosen
20 from styrene resins, PPO and polycarbonate. According to a preferred embodiment, the compositions also comprise a vinyl polymer functionalized by a carboxylic acid, which may, for example, be a polystyrene modified by methacrylic acid.

The prior art shows either blends (i) of styrene resin and
25 polyetheresteramide without a compatibilizer, or blends (ii) of polyetheresteramide and functionalized styrene resin, or else blends (iii) of polyetheresteramide, non-functionalized styrene resin and functionalized styrene resin.

30 [The technical problem]

The blends (i) are antistatic if the polyetheresteramide is properly chosen, but they have poor mechanical properties – in particular, the elongation at break is very much less than that of the styrene resin by itself.

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As regards the blends (ii) and (iii), it is necessary to use a functionalized styrene resin which is complicated and expensive. The aim of the invention is to render antistatic the ordinary styrene resins used for making the abovementioned articles, these resins not being functionalized. It has now
 5 been discovered that, by using particular compatibilizers, it is possible to obtain antistatic styrene resin compositions which retain the properties of the base styrene resin and even have a markedly improved elongation at break.

10 [Brief description of the invention]

The present invention relates to a composition comprising, per 100 parts by weight :

- 99 to 60 parts of a styrene polymer (A),
 - 15 - 1 to 40 parts of (B) + (C),
- (B) being a copolymer containing polyamide blocks and polyether blocks comprising essentially ethylene oxide units $\text{---}(\text{C}_2\text{H}_4\text{---O})\text{---}$,
- (C) being a compatibilizer chosen from low-mass copolymers (C1) of styrene and of an unsaturated carboxylic acid anhydride, copolymers (C2)
 20 of ethylene and of an unsaturated carboxylic acid anhydride and copolymers (C3) of ethylene and of an unsaturated epoxy, blocks copolymers (C4) SBS or SIS grafted by an unsaturated carboxylic acid or an unsaturated carboxylic acid anhydride and mixtures thereof,
- (B)/(C) being between 2 and 10.

25

[Detailed description of the invention]

By way of example of styrene polymer (A), mention may be made of polystyrene, elastomer-modified polystyrene, styrene-acrylonitrile
 30 copolymers (SAN), elastomer-modified SAN, particularly ABS which is obtained, for example, by grafting (graft polymerization) of styrene and acrylonitrile on a polybutadiene or butadiene-acrylonitrile copolymer backbone, and blends of SAN and ABS. The abovementioned elastomers may be, for example, EPR (the abbreviation for ethylene-propylene rubber

or ethylene-propylene elastomer), EPDM (the abbreviation for ethylene-propylene-diene rubber or ethylene-propylene-diene elastomer), polybutadiene, acrylonitrile-butadiene copolymer, polyisoprene or isoprene-acrylonitrile copolymer.

5 In the polymers (A) that have just been mentioned, part of the styrene may be replaced with unsaturated monomers copolymerizable with styrene; by way of example, mention may be made of alpha-methylstyrene and (meth)acrylic esters. As examples of styrene copolymers, mention may also be made of chloropolystyrene, poly-alpha-methylstyrene, styrene-
10 chlorostyrene copolymers, styrene-propylene copolymers, styrene-butadiene copolymers, styrene-isoprene copolymers, styrene-vinyl chloride copolymers, styrene-vinyl acetate copolymers, styrene-alkyl acrylate (methyl, ethyl, butyl, octyl or phenyl acrylate) copolymers, styrene-alkyl methacrylate (methyl, ethyl, butyl or phenyl methacrylate) copolymers,
15 styrene-methyl chloroacrylate copolymers and styrene-acrylonitrile-alkyl acrylate copolymers. In these copolymers, the comonomer content will generally be up to 20% by weight. The present invention also relates to metallocene polystyrenes having a high melting point.

 It would not be outside the scope of the invention if (A) were a blend
20 of two or more of the above polymers.

The polymers (B) containing polyamide blocks and polyether blocks result from the copolycondensation of polyamide blocks having reactive end groups with polyether blocks having reactive end groups, such as, *inter alia* :

- 25 1) polyamide blocks having diamine chain ends with polyoxyalkylene blocks having dicarboxylic chain ends ;
- 2) polyamide blocks having dicarboxylic chain ends with polyoxyalkylene blocks having diamine chain ends obtained by cyanoethylation and hydrogenation of aliphatic
30 dihydroxylated alpha,omega-polyoxyalkylene blocks called polyetherdiols ;
- 3) polyamide blocks having dicarboxylic chain ends with polyetherdiols, the products obtained being, in this particular

case, polyetheresteramides. The copolymers (B) are advantageously of this type.

The polyamide blocks having dicarboxylic chain ends stem, for example, from the condensation of alpha,omega-aminocarboxylic acids, of lactams or of dicarboxylic acids and diamines in the presence of a chain-stopper dicarboxylic acid.

The number-average molar mass \overline{M}_n of the polyamide blocks is between 300 and 15,000 and preferably between 600 and 5000. The mass \overline{M}_n of the polyether blocks is between 100 and 6000 and preferably between 200 and 3000.

The polymers containing polyamide blocks and polyether blocks may also include randomly distributed units. These polymers may be prepared by the simultaneous reaction of the polyether and of the polyamide-block precursors.

For example, it is possible to react a polyetherdiol, a lactam (or an alpha,omega-amino acid) and a chain-stopper diacid in the presence of a little water. What is obtained is a polymer having essentially polyether blocks and polyamide blocks of very variable length but also the various reactants which, having reacted randomly, are distributed randomly along the polymer chain.

These polymers containing polyamide blocks and polyether blocks, which stem from the copolycondensation of polyamide and polyether blocks prepared beforehand or from a one-step reaction, have, for example, Shore D hardnesses which may be between 20 and 75, advantageously between 30 and 70, and an intrinsic viscosity between 0.8 and 2.5 measured in metacresol at 250°C for an initial concentration of 0.8 g/100 ml. The MFI values may be between 5 and 50 (235°C under a load of 1 kg).

The polyetherdiol blocks are either used as they are and copolycondensed with polyamide blocks having carboxylic end groups, or they are aminated in order to be converted into polyetherdiamines and condensed with polyamide blocks having carboxylic end groups. They may also be mixed with polyamide precursors and a chain stopper in order to

make the polymers containing polyamide blocks and polyether blocks having randomly distributed units.

Polymers containing polyamide blocks and polyether blocks are described in Patents US 4,331,786, US 4,115,475, US 4,195,015,
 5 US 4,839,441, US 4,864,014, US 4,230,838 and US 4,332,920.

According to a first embodiment of the invention, the polyamide blocks having dicarboxylic chain ends stem, for example, from the condensation of alpha,omega-aminocarboxylic acids, of lactams or of dicarboxylic acids and diamines in the presence of a chain-stopper
 10 dicarboxylic acid. By way of example of alpha,omega-aminocarboxylic acids mention may be made of aminoundecanoic acid, by way of example of lactams mention may be made of caprolactam and lauryllactam, by way of example of dicarboxylic acids mention may be made of adipic acid, decanedioic acid and dodecanedioic acid and by way of example of a
 15 diamine mention may be made of hexamethylene diamine. Advantageously, the polyamide blocks are of nylon-12 (PA 12) or of nylon-6 (PA 6). The melting point of these polyamide blocks, which is also that of the copolymer (B), is generally 10 to 15°C below that of PA 12 or of PA 6.

Depending on the nature of (A), it may be useful to use a copolymer
 20 (B) having a lower melting point so as not to degrade (A) during the incorporation of (B), this being the subject of the second and third embodiments below.

According to a second embodiment of the invention, the polyamide blocks result from the condensation of one or more alpha,omega-aminocarboxylic acids and/or of one or more lactams having from 6 to 12
 25 carbon atoms in the presence of a dicarboxylic acid having from 4 to 12 carbon atoms and have a low mass, that is to say \overline{M}_n of 400 to 1000. By way of example of alpha,omega-aminocarboxylic acids, mention may be made of aminoundecanoic acid and aminododecanoic acid. By way of
 30 example of dicarboxylic acids, mention may be made of adipic acid, sebacic acid, isophthalic acid, butanedioic acid, 1,4-cyclohexyldicarboxylic acid, terephthalic acid, the sodium or lithium salt of sulphisophthalic acid, dimerized fatty acids (these dimerized fatty acids have a dimer content of at

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least 98% and are preferably hydrogenated) and dodecanedioic acid $\text{HOOC}-(\text{CH}_2)_{10}-\text{COOH}$.

By way of example of lactams, mention may be made of caprolactam and lauryllactam.

- 5 Caprolactam should be avoided unless the polyamide is purified of the caprolactam monomer which remains dissolved in it.

Polyamide blocks, obtained by the condensation of lauryllactam in the presence of adipic acid or of dodecanedioic acid, have a mass \overline{M}_n of 750 and a melting point of 127 – 130°C.

- 10 According to a third embodiment of the invention, the polyamide blocks result from the condensation of at least one alpha,omega-aminocarboxylic acid (or a lactam), at least one diamine and at least one dicarboxylic acid. The alpha,omega-aminocarboxylic acid, the lactam and the dicarboxylic acid may be chosen from those mentioned above.

- 15 The diamine may be an aliphatic diamine having from 6 to 12 atoms or it may be an aryl diamine and/or a saturated cyclic diamine.

- By way of examples, mention may be made of hexamethylenediamine, piperazine, 1-aminoethylpiperazine, bis(amino-propyl)piperazine, tetramethylenediamine, octamethylenediamine, deca-
20 methylenediamine, dodecamethylenediamine, 1,5-diaminohexane, 2,2,4-trimethyl-1,6-diaminohexane, diamine polyols, isophoronediamine(IPDA), methylpentamethylenediamine (MPDM), bis(aminocyclohexyl)methane (BACM) and bis(3-methyl-4-aminocyclohexyl)methane (BMACM).

- In the second and third embodiments of the invention, the various
25 constituents of the polyamide block and their proportion are chosen so as to obtain a melting point of less than 150°C and advantageously of between 90 and 135°C. Low-melting-point copolyamides are described in Patents US 4,483,975, DE 3,730,504 and US 5,459,230 and the same proportions of the constituents are used for the polyamide blocks of (B). (B)
30 may also be the copolymers described in US 5, 489,667.

The polyether blocks may represent from 5 to 85% by weight of (B). The polyether blocks may contain units other than ethylene oxide units, such as, for example, propylene oxide or polytetrahydrofuran (which leads

to polytetramethylene glycol chain linkages). It is also possible to use, simultaneously, PEG blocks, i.e. those consisting of ethylene oxide units, PPG blocks, i.e. those consisting of propylene oxide units, and PTMG blocks, i.e. those consisting of tetramethylene glycol units also called polytetrahydrofuran. Advantageously, PEG blocks or blocks obtained by the oxyethylation of bisphenols, such as bisphenol A for example, may be used. The latter products are described in Patent EP 613,919. The amount of polyether blocks in (B) is advantageously from 10 to 50% by weight of (B) and preferably from 35 to 50%.

10 The copolymers of the invention may be prepared by any means allowing the polyamide blocks and the polyether blocks to be linked together. In practice, essentially two processes are used, one being called a two-step process and the other a one-step process.

The two-step process firstly consists in preparing the polyamide blocks having carboxylic end groups by the condensation of polyamide precursors in the presence of a chain-stopper dicarboxylic acid and then, in a second step, in adding the polyether and a catalyst. If the polyamide precursors are only lactams or alpha,omega-aminocarboxylic acids, a dicarboxylic acid is added. If the precursors already comprise a dicarboxylic acid, this is used in excess with respect to the stoichiometry of the diamines. The reaction usually takes place between 180 and 300°C, preferably 200 to 260°C, and the pressure in the reactor is set between 5 and 30 bar and maintained for approximately 2 hours. The pressure in the reactor is slowly reduced to atmospheric pressure and then the excess water is distilled off, for example for one or two hours.

Once the polyamide having carboxylic acid end groups has been prepared, the polyether and a catalyst are then added. The polyether may be added in one or more goes, and likewise for the catalyst. According to one advantageous embodiment, the polyether is added first and the reaction of the OH end groups of the polyether with the COOH ends of the polyamide starts, with the formation of ester linkages and the elimination of water. The water is removed as much as possible from the reaction mixture by distillation and then the catalyst is introduced in order to complete the linking of the polyamide blocks to the polyether blocks. This second step

takes place with stirring, preferably under a vacuum of at least 5 mmHg (650 Pa) at a temperature such that the reactants and the copolymers obtained are in the molten state. By way of example, this temperature may be between 100 and 400°C and usually between 200 and 300°C. The reaction is monitored by measuring the torsional moment, or torque, exerted by the polymer melt on the stirrer or by measuring the electric power consumed by the stirrer. The end of the reaction is determined by the value of the torque or of the target power. The catalyst is defined as being any product which promotes the linking of the polyamide blocks to the polyether blocks by esterification. Advantageously, the catalyst is a derivative of a metal (M) chosen from the group formed by titanium, zirconium and hafnium.

By way of example of derivatives, mention may be made of tetraalkoxides which satisfy the general formula $M(OR)_4$, in which M represents titanium, zirconium or hafnium and the Rs, which are identical or different, denote linear or branched, alkyl radicals having from 1 to 24 carbon atoms.

The C_1 to C_{24} alkyl radicals from which the radicals R of the tetraalkoxides used as catalysts in the process according to the invention are chosen are, for example, such as methyl, ethyl, propyl, isopropyl, butyl, ethylhexyl, decyl, dodecyl and hexadodecyl. The preferred catalysts are tetraalkoxides for which the radicals R, which are identical or different, are C_1 to C_8 alkyl radicals. Examples of such catalysts are especially $Zr(OC_2H_5)_4$, $Zr(O\text{-}isoC_3H_7)_4$, $Zr(OC_4H_9)_4$, $Zr(OC_5H_{11})_4$, $Zr(OC_6H_{13})_4$, $Hf(OC_2H_5)_4$, $Hf(OC_4H_9)_4$ and $Hf(O\text{-}isoC_3H_7)_4$.

The catalyst used in this process according to the invention may consist only of one or of several of the tetraalkoxides of formula $M(OR)_4$ defined above. It may also be formed by the combination of one or more of these tetraalkoxides with one or more alkali or alkaline-earth metal alcoholates of formula $(R_1O)_pY$ in which R_1 denotes a hydrocarbon residue, advantageously a C_1 to C_{24} alkyl residue and preferably a C_1 to C_8 alkyl residue, Y represents an alkali or alkaline-earth metal and p is the valency of Y. The amounts of alkali or alkaline-earth metal alcoholate and of

zirconium or hafnium tetraalkoxides which are combined to form the mixed catalyst may vary within wide limits. However, it is preferred to use amounts of alcoholate and of tetraalkoxides so that the molar proportion of alcoholate is approximately equal to the molar proportion of tetraalkoxide.

5 The weight proportion of catalyst, that is to say of the tetraalkoxide(s), when the catalyst does not contain an alkali or alkaline-earth metal alcoholate, or else of all of the tetraalkoxide(s) and of the alkali or alkaline-earth metal alcoholate(s) when the catalyst is formed by the combination of these two types of compounds, advantageously varies from
10 0.01 to 5% of the weight of the mixture of the dicarboxylic polyamide with the polyoxyalkylene glycol, and preferably lies between 0.05 and 2% of this weight.

By way of example of other derivatives, mention may also be made of the salts of the metal (M), particularly the salts of (M) and an organic acid
15 and the complex salts between the oxide of (M) and/or the hydroxide of (M) and an organic acid. Advantageously, the organic acid may be formic acid, acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, caprylic acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, carboxylic cyclohexane acid, phenylacetic acid, benzoic
20 acid, salicylic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid, fumaric acid, phthalic acid and crotonic acid. Acetic and propionic acids are particularly preferred. Advantageously M is zirconium. These salts may be called zirconyl salts. The Applicant believes that these salts of zirconium and of an organic acid or the complex salts
25 mentioned above release ZrO^{++} during the process, without being bound by this explanation. The product used is the one sold under the name zirconyl acetate. The amount to be used is the same as for the $M(OR)_4$ derivatives.

This process and these catalysts are described in Patents
US 4,332,920, US 4,230,838, US 4,331,786, US 4,252,920, JP
30 07145368A, JP 06287547A and EP 613919.

With regard to the one-step process, all the reactants used in the two-step process, that is to say the polyamide precursors, the chain-stopper dicarboxylic acid, the polyether and the catalyst, are mixed together. They are the same reactants and the same catalyst as in the two-

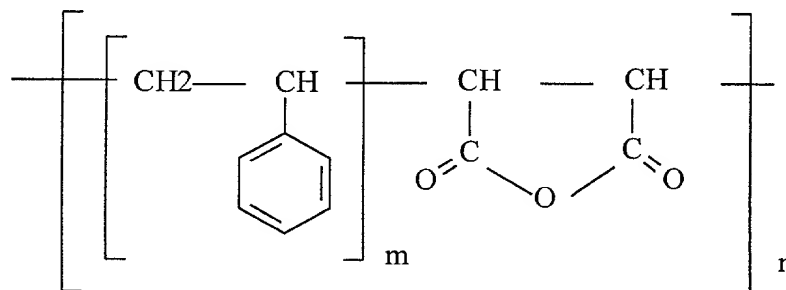
step process described above. If the polyamide precursors are only lactams, it is advantageous to add a little water.

The copolymer has essentially the same polyether blocks and the same polyamide blocks, but also a small portion of the various reactants
5 that have reacted randomly, which are distributed randomly along the polymer chain.

As in the first step of the two-step process described above, the reactor is closed and heated, with stirring. The pressure established is between 5 and 30 bar. When the pressure no longer changes, the reactor
10 is put under reduced pressure while still maintaining vigorous stirring of the molten reactants. The reaction is monitored as previously in the case of the two-step process.

The catalyst used in the one-step process is preferably a salt of the metal (M) and of an organic acid or a complex salt between the oxide
15 and/or hydroxide of (M) and an organic acid.

With regard to the compatibilizers (C1), the unsaturated carboxylic acid anhydride may be chosen, for example, from maleic, itaconic, citraconic, allyl succinic, cyclohex-4-ene-1,2-dicarboxylic, 4-methylenecyclohex-4-ene-1,2-dicarboxylic, bicyclo(2,2,1)hept-5-ene-2,3-dicarboxylic
20 and x-methylbicyclo(2,2,1)hept-5-ene-2,2-dicarboxylic anhydrides. Advantageously, maleic anhydride is used. The number-average molar mass is between 800 and 10,000 and preferably between 1000 and 3500. (C1) may be represented by the following formula :



in which MAH denotes maleic anhydride, m varies from 1 to 3 and n varies from 6 to 8. These copolymers may be partially esterified, between

35 and 75%, by alcohols. These products are sold under the name SMA[®] RESINS by Elf Atochem.

5 **With regard to the compatibilizers (C2)**, these may be polyethylenes grafted by an unsaturated carboxylic acid anhydride or copolymers of ethylene and of an unsaturated carboxylic acid anhydride obtained, for example, by radical polymerization.

With regard to the polyethylenes onto which the unsaturated carboxylic acid anhydride is grafted, these should be understood to mean the polyethylene of homopolymers or copolymers.

10 By way of comonomers, mention may be made of :

- alpha-olefins, advantageously those having from 3 to 30 carbon atoms ; by way of example of alpha-olefins, mention may be made of propylene, 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 15 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicocene, 1-dococene, 1-tetracocene, 1-hexacocene, 1-octacocene and 1-triacontene; these alpha-olefins may be used by themselves or as a mixture of two or more of them ;

- the esters of unsaturated carboxylic acids, such as, for example, 20 alkyl (meth)acrylates, the alkyls possibly having up to 24 carbon atoms ; examples of alkyl acrylates or methacrylates are, especially, methyl methacrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate and 2-ethylhexyl acrylate;

- vinyl esters of saturated carboxylic acids, such as, for example, 25 vinyl acetate or vinyl propionate ;

- dienes such as, for example, 1,4-hexadiene.

The polyethylene may include several comonomers.

Advantageously, the polyethylene, which may be a blend of several polymers, comprises at least 50 mol% and preferably 75 mol% of ethylene 30 and its density may be between 0.86 and 0.98 g/cm³. The MFI (viscosity index at 190°C/2.16 kg) is advantageously between 1 and 1000 g/10 min.

By way of example of polyethylenes, mention may be made of :

- low-density polyethylene (LDPE) ;
- high-density polyethylene (HDPE) ;

- linear low-density polyethylene (LLDPE) ;
- very low-density polyethylene (VLDPE) ;
- polyethylene obtained by metallocene catalysis, that is to say

5 such as propylene, butene, hexene or octene in the presence of a single-site catalyst generally consisting of a zirconium or titanium atom and of two alkyl cyclic molecules linked to the metal. More specifically, metallocene catalysts are usually composed of two cyclopentadiene rings linked to the metal. These catalysts are frequently used with aluminoxanes as
10 cocatalysts or activators, preferably methyl aluminoxane (MAO). Hafnium may also be used as the metal to which the cyclopentadiene is fixed. Other metallocenes may include transition metals of Groups IVA, VA and VIA. Metals from the series of lanthanides may also be used ;

- EPR (ethylene - propylene - rubber) elastomers ;
- 15 - EPDM (ethylene - propylene – diene monomer) elastomers ;
- blends of polyethylene with an EPR or an EPDM ;
- ethylene-alkyl (meth)acrylate copolymers possibly containing up to 60%, and preferable 2 to 40%, by weight of (meth)acrylate.

The grafting is an operation known per se.

20 With regard to the copolymers of ethylene and unsaturated carboxylic acid anhydride, that is to say those in which the unsaturated carboxylic acid anhydride is not grafted, these are copolymers of ethylene, unsaturated carboxylic acid anhydride and possible another monomer which may be chosen from the comonomers mentioned above in the case
25 of the ethylene copolymers intended to be grafted.

Advantageously, ethylene-maleic anhydride and ethylene-alkyl (meth)acrylate-maleic anhydride copolymers are used. These copolymers comprise from 0.2 to 10% by weight of maleic anhydride and from 0 to 40% by weight of alkyl (meth)acrylate. Their MFI is between 1 and 50 (190°C –
30 2.16 kg). The alkyl (meth)acrylates have already been described above.

It would not be outside the scope of the invention to replace the unsaturated carboxylic acid anhydride in (C2) with an unsaturated carboxylic acid such as (meth)acrylic acid, this functional group possibly being partially neutralized by a metal (Zn) or an alkali metal (Li), giving, in

With regard to the compatibilizers (C3), the copolymer of ethylene and an unsaturated epoxy may be obtained by copolymerizing ethylene with an unsaturated epoxy or by grafting the unsaturated epoxy onto the polyethylene. The grafting may be carried out in a solvent phase or on the polyethylene melt in the presence of a peroxide. These grafting techniques are known per se. As regards the copolymerization of ethylene with an unsaturated epoxy, the so-called radical polymerization processes may be used, these normally being carried out at pressures between 200 and 2500 bar.

- aliphatic glycidyl esters and ethers, such as allyl glycidyl ether, vinyl glycidyl ether, glycidyl maleate and itaconate, and glycidyl (meth)acrylate ; and
- alicyclic glycidyl esters and ethers, such as 2-cyclohexene-1-yl-glycidyl ether, diglycidyl cyclohexene-4,5-carboxylate, glycidyl cyclohexene-4-carboxylate, glycidyl 2-methyl-5-norbornene-2-carboxylate and diglycidyl *endo-cis*-bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylate.

Advantageously, the compatibilizer (C3) is an ethylene/alkyl (meth)acrylate/unsaturated epoxy copolymer. Advantageously it may contain up to 40% by weight of alkyl (meth)acrylate and up to 10%, preferably 0.1 to 8%, by weight of unsaturated epoxy.

Advantageously, the alkyl (meth)acrylate is chosen from methyl (meth)acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate and 2-ethylhexyl acrylate. The amount of alkyl (meth)acrylate is advantageously

from 20 to 35%. The MFI is advantageously between 1 and 50 (in g/10 min at 190°C under 2.16 kg). This copolymer may be obtained by the radical polymerization of the monomers.

With regard to the compatibilizers (C4), they are polystyrene / polybutadiene / polystyrene copolymers (SBS), polystyrene / polyisoprene / polystyrene copolymers (SIS), they can be hydronenated. It means they can be polystyrene / poly(ethylene-butene) / polystyrene copolymers (SEBS), polystyrene / poly(ethylene-propylene) / polystyrene copolymers (SEPS). Such block copolymers are described in Ullmann's Encyclopedia of Industrial Chemistry, Vol A 26, pages 655-663, fifth édition, 1995. These block copolymers are grafted by acrylic acid or maleic anhydride.

It would not be outside the scope of the invention to use one or more compatibilizers (C1), one or more compatibilizers (C2), one or more compatibilizers (C3), one or more compatibilizers (C4) or a mixture of at least two of these compatibilizers.

The antistatic behaviour increases with the proportion of (B) and, for equal amounts of (B), with the proportion of ethylene oxide units contained in (B).

The amount of (B) + (C) is advantageously from 5 to 20 parts per 95 to 80 parts of (A) and preferably from 10 to 15 parts per 90 to 85 parts of (A). The ratio (B)/(C) is advantageously between 4 and 6.

It would not be outside the scope of the invention to add mineral fillers (talc, CaCO_3 , kaolin, etc.), reinforcing agents (glass fibre, mineral fibre, carbon fibre, etc.), stabilizers (heat stabilizers and UV stabilizers), fire retardants and colorants.

The compositions of the invention are prepared by the usual techniques for thermoplastics, such as, for example, by extrusion or with the aid of twin-screw mixers.

The present invention also relates to articles manufactured from the above compositions ; these are, for example, films, tubes or pipes, sheets, packaging, and computer or telephone casings.

[Examples]

In the examples below, the following ingredients are used :

- **PS**: this is an impact polystyrene. This copolymer is characterized by a melt flow index at 200°C under 5 kg of between 3 and 5 g/10 min (ISO 1133:91 standard). It is also characterized by a Vicat temperature of 97°C (ISO 306A50 standard) and an Izod impact strength (ISO 180/1A standard) of 10 kJ/m². It is sold by Elf Atochem under the reference LACQRENE®4241.
- **Pebax®**: this is a copolyether-block-amide having nylon-12 blocks of 1500 number-average molar mass and PEG blocks of 1500 number-average molar mass; the MFI is 14 at 235°C/1 kg and the melting point is 158°C.
- **Lotader® AX**: ethylene-methyl acrylate-glycidyl methacrylate terpolymer. This terpolymer has an MFI of 6 (190°C/325 g) and a melting point of 63°C.
- **SMA®2625**: partially esterified styrene-maleic anhydride copolymer (such that m = 2 in the abovementioned formula), of 1900 average molar mass, having a melting range of 135 – 150°C and an acid number between 200 and 240 mg KOH/g.
- **Orevac®**: ethylene-methyl acrylate copolymer grafted with maleic anhydride. This product has a melting point of 65°C and an MFI of 3.5 under 190°C/2.16 kg conditions.

In the examples which follow, the following characterization techniques were used:

- Mechanical properties:
- 25 The compositions obtained were injection moulded at temperatures of 200 to 220°C in the form of dumb bells or plaques. The dumb bells allow the tensile tests to be carried out according to the ISO R527 standard.
- Antistatic properties:
- 30 Plaques of dimensions 100 mm × 100 mm × 2 mm are injection moulded and allow the resistivity measurements to be carried out according to the IEC-93 standard. The surface resistivity is measured in ohms/□ and the half-discharged time (CDT) in seconds; the properties obtained under tension are also given. All the tests are carried out at 23°C. The plaques

are conditioned at 50% humidity for 15 days before being tested in the case of the surface resistivity measurement.

Examples 1 to 5

- 5 A Buss co-kneader of length equal to eleven times the diameter (Buss 11D) with a total throughput of 25 kg/h is used. This throughput represents the sum of the throughputs of the ingredients used. The temperature settings of the barrels are those normally used for a polystyrene, that is to say from 200 to 220°C. The strands output by the
- 10 machine are cooled in a water tank and converted into granules. These granules are injection moulded in the form of plaques or dumb bells at a temperature of between 220 and 240°C. The results are given in Table 1 below.

TABLE 1

PS	100	90	88	88	88	88
Pebax		10	10	10	110	10
Orevac			2			
SMA 2625				2		1
Lotader AX					2	1
$R_s (\Omega/\square)$	$1.6 \cdot 10^{+15}$	$8.0 \cdot 10^{+12}$	$3.0 \cdot 10^{+12}$	$4.0 \cdot 10^{+12}$	$3.0 \cdot 10^{+12}$	$3.0 \cdot 10^{+12}$
CDT (s)	53	4	4	3	6	4
Yield stress (MPa)	30.4	27.4	27.6	28	27.5	27.9
Yield strain (%)	1.4	1.6	1.6	1.6	1.6	1.6
Tensile strength (MPa)	23.6	19.6	21.9	22.3	22.6	22.9
Elongation at break (%)	34	12	43	40	57	56

CLAIMS

- 1 Composition comprising, per 100 parts by weight :
 - 99 to 60 parts of a styrene polymer (A),
 5 - 1 to 40 parts of (B) + (C),
 (B) being a copolymer containing polyamide blocks and polyether blocks comprising essentially ethylene oxide units $-(C_2H_4-O)-$,
 (C) being a compatibilizer chosen from low-mass copolymers (C1) of styrene and of an unsaturated carboxylic acid anhydride, copolymers (C2)
 10 of ethylene and of an unsaturated carboxylic acid anhydride and copolymers (C3) of ethylene and of an unsaturated epoxy, blocks copolymers (C4) SBS or SIS grafted by an unsaturated carboxylic acid or an unsaturated carboxylic acid anhydride and mixtures thereof,
 (B)/(C) being between 2 and 10.
- 15
- 2 Composition according to Claim 1, in which (A) is polystyrene.
- 3 Composition according to Claim 1, in which (A) is ABS.
- 20
- 4 Composition according to any one of the preceding claims, in which (C1) is a copolymer of styrene and maleic anhydride, having an average molar mass of between 800 and 10,000.
- 5 Composition according to any one of Claims 1 to 3, in which
 25 (C2) is chosen from ethylene-alkyl (meth)acrylate-maleic anhydride copolymers, these copolymers containing from 0.2 to 10% by weight of maleic anhydride and from 0 to 40% by weight of alkyl (meth)acrylate.
- 6 Composition according to any one of Claims 1 to 3, in which
 30 (C3) is advantageously an ethylene/alkyl (meth)acrylate/unsaturated epoxy copolymer possibly containing up to 40% by weight of alkyl(meth)acrylate and up to 10% by weight of unsaturated epoxy.

7 Composition according to any one of the preceding claims, in which the amount of (B) + (C) is advantageously from 5 to 20 parts per 95 to 80 parts of (A).

5 8 Composition according to any one of the preceding claims, in which the ratio (B)/(C) is between 4 and 6.

9 Articles manufactured from a composition according to any one of the preceding claims.

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ABSTRACT

□□□□□

ANTISTATIC STYRENE POLYMER COMPOSITIONS

□□□□□

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Agent : Henry NÉEL

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Inventors : M. Christophe LACROIX

□□□□□

The present invention relates to a composition comprising, per 100 parts by weight :

- 99 to 60 parts of a styrene polymer (A),
- 1 to 40 parts of (B) + (C),

(B) being a copolymer containing polyamide blocks and polyether blocks comprising essentially ethylene oxide units $-(C_2H_4-O)-$,

(C) being a compatibilizer chosen from low-mass copolymers (C1) of styrene and of an unsaturated carboxylic acid anhydride, copolymers (C2) of ethylene and of an unsaturated carboxylic acid anhydride and copolymers (C3) of ethylene and of an unsaturated epoxy, blocks copolymers (C4) SBS or SIS grafted by an unsaturated carboxylic acid or an unsaturated carboxylic acid anhydride and mixtures thereof,

(B)/(C) being between 2 and 10.

DECLARATION FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

ANTISTATIC STYRENE POLYMER COMPOSITIONS

the specification of which

☐ is attached hereto

☒ was filed on 26 JULY 2000 as United States Application Number or PCT International Application Number PCT/FR00/02140 and (if applicable) was amended on _____

I hereby authorize our attorneys to insert the serial number assigned to this application.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 USC §119			
APPLICATION NO.	COUNTRY	DAY/MONTH/YEAR FILED	PRIORITY CLAIMED
99/10125	FRANCE	4 AUGUST 1999	YES

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below.

PROVISIONAL APPLICATION(S) UNDER 35 U.S.C. §119(e)	
APPLICATION NUMBER	FILING DATE

I hereby claim the benefit under 35 U.S.C. §120 of any United States application, or §365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. §112.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

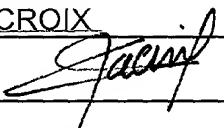
PRIOR U.S./PCT INTERNATIONAL APPLICATION(S) DESIGNATED FOR BENEFIT UNDER 37 U.S.C. §120		
APPLICATION NO.	FILING DATE	STATUS — PATENTED, PENDING, ABANDONED

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected herewith: I. William Millen (19,544); John L. White (17,746); Anthony J. Zelano (27,969); Alan E.J. Branigan (20,565); John R. Moses (24,983); Harry B. Shubin (32,004); Brion P. Heaney (32,542); Richard J. Traverso (30,595); John A. Sopp (33,103); Richard M. Lebovitz (37,067); John H. Thomas (33,460); Catherine M. Joyce (40,668); Nancy J. Axelrod (44,014); James T. Moore (35,619); James E. Ruland (40,921) and Jennifer J. Branigan (37,432)

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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☐ Additional joint inventors are named on separately numbered sheets attached hereto.